Berry's Geometric Phase

Introductory Lecture

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The landmark paper, 1983-1984

Proc. R. Soc. Lond. A **392**, 45–57 (1984)
Printed in Great Britain

Quantal phase factors accompanying adiabatic changes

BY M. V. BERRY, F.R.S.
H. H. Wills Physics Laboratory, University of Bristol, Tyndall Avenue, Bristol BS8 1TL, U.K.

(*Received* 13 *June* 1983)

- Very simple concept, nonetheless missed by the founding fathers of QM in the 1920s and 1930s
- Nowadays in any modern elementary QM textbook

Sakurai QM textbook, p. 464

SUPPLEMENT I

Adiabatic Change and Geometrical Phase

When the author died in 1982, this book was left in manuscript form; subsequently, there have been some new developments in quantum mechanics. The most important development is a definitive formulation of geometrical phases, introduced by M. V. Berry in 1983. The phase factors accompanying adiabatic changes are expressed in concise and elegant forms and have found universal applications in various fields of physics, thus giving a new viewpoint to quantum theory. We review here the physical consequences of these phases, which have in fact been used unconsciously in some cases already, by adding a supplement to the Japanese version of the text. (Here in the new English edition of *Modern Quantum Mechanics* we are providing a translation from Japanese of this supplement, prepared by Professor Akio Sakurai of Kyoto Sangyo University for the Japanese version of the book. The Editor deeply appreciates Professor Akio Sakurai's guidance on an initial translation provided by his student, Yasunaga Suzuki, as a term paper for the graduate quantum mechanics course here at the University of Hawaii—Manoa.)

Outline

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Is this a paradox?

SECOND SERIES, VOL. 115, NO. 3 AUGUST 1, 1959

Significance of Electromagnetic Potentials in the Quantum Theory

Y. AHARONOV AND D. BOHM
H. H. Wills Physics Laboratory, University of Bristol, Bristol, England
(Received May 28, 1959; revised manuscript received June 16, 1959)

In this paper, we discuss some interesting properties of the electromagnetic potentials in the quantum domain. We shall show that, contrary to the conclusions of classical mechanics, there exist effects of potentials on charged particles, even in the region where all the fields (and therefore the forces on the particles) vanish. We shall then discuss possible experiments to test these conclusions; and, finally, we shall suggest further possible developments in the interpretation of the potentials.

Feynman Lectures (1962-63), Vol. 2, Sec 15-5

Nowadays free online at `http://www.feynmanlectures.caltech.edu`

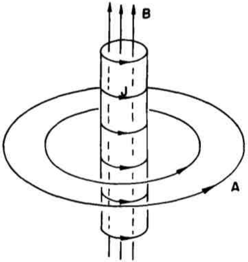


Fig. 15–6. The magnetic field and vector potential of a long solenoid.

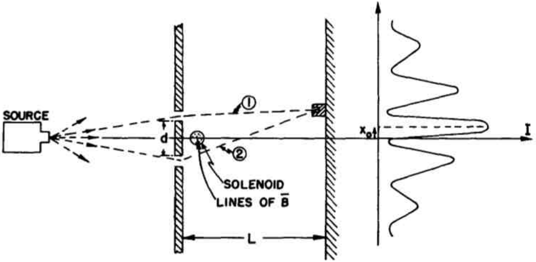


Fig. 15–7. A magnetic field can influence the motion of electrons even though it exists only in regions where there is an arbitrarily small probability of finding the electrons.

"...**E** and **B** are slowly disappearing from the modern expression of physical laws; they are being replaced by **A** and Φ".

Feynman vs. the bad guys....

IL NUOVO CIMENTO VOL. 47 A, N. 4 21 Ottobre 1978

Nonexistence of the Aharonov-Bohm Effect.

P. BOCCHIERI

Istituto di Fisica Teorica dell'Università - Pavia, Italia
Istituto Nazionale di Fisica Nucleare - Sezione di Pavia, Italia

A. LOINGER

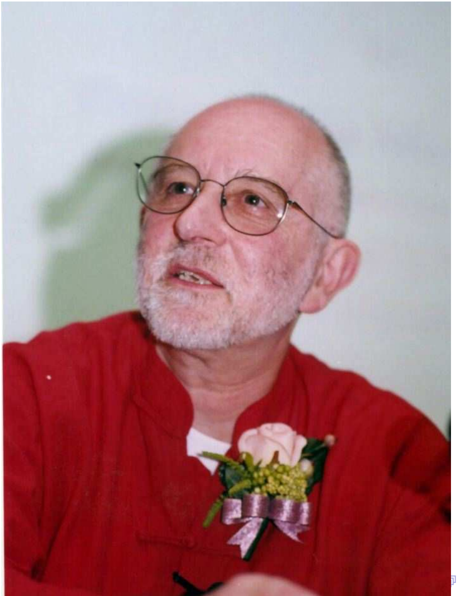
Istituto di Scienze Fisiche dell'Università - Milano, Italia

(ricevuto il 2 Giugno 1978)

Summary. — In this paper the Aharonov-Bohm effect is investigated and it is shown that it has a purely mathematical origin. All the physical consequences of quantum mechanics turn out to be dependent on the field strengths and not on the potentials.

Outline

Professor Sir Michael Berry, FRS



Berry knighted by the queen

Ig Nobel award, 2000: M. Berry & A. Geim

...the physics prize, awarded to Andre Geim of the University of Nijmegen (the Netherlands) and Sir Michael Berry of Bristol University (UK), for using magnets to levitate a frog.

More info:
"Of Flying Frogs and Levitrons" by M.V. Berry and A.K. Geim, European Journal of Physics, v. 18, 1997, p. 307-13.

Movies of levitating frogs


image courtesy University of Nijmegen

Berry's reaction at his website:
"We are pleased to accept the Ig prize because we have always considered it a duty to make physics more understandable and bring it closer to nonscientists. We think the prize acknowledges our contribution in this direction...."

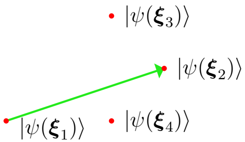
The real Nobel award, 2010

Andre Geim

Basics

Parametric Hamiltonian, non degenerate ground state

$$H(\xi)|\psi(\xi)\rangle = E(\xi)|\psi(\xi)\rangle \qquad \text{parameter } \xi\text{: “slow variable”}$$



$$e^{-i\Delta\varphi_{12}} = \frac{\langle\psi(\xi_1)|\psi(\xi_2)\rangle}{|\langle\psi(\xi_1)|\psi(\xi_2)\rangle|}$$

$$\Delta\varphi_{12} = -\,\mathrm{Im}\log\langle\psi(\xi_1)|\psi(\xi_2)\rangle$$

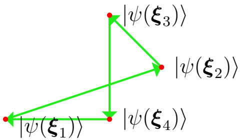
$$\begin{aligned}\gamma &= \Delta\varphi_{12} + \Delta\varphi_{23} + \Delta\varphi_{34} + \Delta\varphi_{41} \\ &= -\,\mathrm{Im}\log\langle\psi(\xi_1)|\psi(\xi_2)\rangle\langle\psi(\xi_2)|\psi(\xi_3)\rangle\langle\psi(\xi_3)|\psi(\xi_4)\rangle\langle\psi(\xi_4)|\psi(\xi_1)\rangle\end{aligned}$$

Gauge-invariant!

Basics

Parametric Hamiltonian, non degenerate ground state

$$H(\xi)|\psi(\xi)\rangle = E(\xi)|\psi(\xi)\rangle \qquad \text{parameter } \xi\text{: "slow variable"}$$



$$e^{-i\Delta\varphi_{12}} = \frac{\langle\psi(\boldsymbol{\xi}_1)|\psi(\boldsymbol{\xi}_2)\rangle}{|\langle\psi(\boldsymbol{\xi}_1)|\psi(\boldsymbol{\xi}_2)\rangle|}$$

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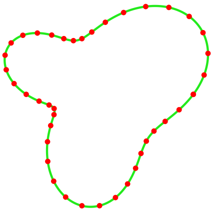
$$= -\operatorname{Im}\log\langle\psi(\boldsymbol{\xi}_1)|\psi(\boldsymbol{\xi}_2)\rangle\langle\psi(\boldsymbol{\xi}_2)|\psi(\boldsymbol{\xi}_3)\rangle\langle\psi(\boldsymbol{\xi}_3)|\psi(\boldsymbol{\xi}_4)\rangle\langle\psi(\boldsymbol{\xi}_4)|\psi(\boldsymbol{\xi}_1)\rangle$$

Gauge-invariant!

From discrete "geometry" to differential geometry

A smooth closed curve C in ξ space



$$e^{-i\Delta\varphi} = \frac{\langle\psi(\boldsymbol{\xi})|\psi(\boldsymbol{\xi}+\Delta\boldsymbol{\xi})\rangle}{|\langle\psi(\boldsymbol{\xi})|\psi(\boldsymbol{\xi}+\Delta\boldsymbol{\xi})\rangle|}$$

If we choose a **differentiable gauge**:

$$-i\Delta\varphi \simeq \langle\psi(\boldsymbol{\xi})|\nabla_{\boldsymbol{\xi}}\psi(\boldsymbol{\xi})\rangle \cdot \Delta\boldsymbol{\xi}$$

$$\gamma = \sum_{s=1}^{M} \Delta\varphi_{s,s+1} \longrightarrow \oint_C d\varphi$$

$$d\varphi = \mathcal{A}(\boldsymbol{\xi}) \cdot d\boldsymbol{\xi} = i\,\langle\psi(\boldsymbol{\xi})|\nabla_{\boldsymbol{\xi}}\psi(\boldsymbol{\xi})\rangle \cdot d\boldsymbol{\xi}$$

$d\varphi$ linear differential form, $\quad i\,\langle\psi(\boldsymbol{\xi})|\nabla_{\boldsymbol{\xi}}\psi(\boldsymbol{\xi})\rangle$ vector field

Berry connection & Berry curvature

- Domain S: $\boldsymbol{\xi} \in S \subset \mathbb{R}^d$

- Berry **connection**
  $\boldsymbol{\mathcal{A}}(\boldsymbol{\xi}) = i \langle \psi(\boldsymbol{\xi}) | \nabla_{\boldsymbol{\xi}} \psi(\boldsymbol{\xi}) \rangle$
  - **real**, nonconservative vector field
  - gauge-dependent
  - "geometrical" vector potential
  - a.k.a. "gauge potential"

- Berry **curvature** $(\boldsymbol{\xi} \in \mathbb{R}^3)$
  $\boldsymbol{\Omega}(\boldsymbol{\xi}) = \nabla_{\boldsymbol{\xi}} \times \boldsymbol{\mathcal{A}}(\boldsymbol{\xi}) = i \langle \nabla_{\boldsymbol{\xi}} \psi(\boldsymbol{\xi}) | \times | \nabla_{\boldsymbol{\xi}} \psi(\boldsymbol{\xi}) \rangle$
  - gauge-invariant (hence observable)
  - geometric analog of a magnetic field
  - a.k.a. "gauge field"

The Berry connection is real

$$\langle\psi(\boldsymbol{\xi})|\psi(\boldsymbol{\xi})\rangle = 1 \qquad \forall\boldsymbol{\xi}$$

$$\begin{aligned}
\nabla_{\boldsymbol{\xi}}\langle\psi(\boldsymbol{\xi})|\psi(\boldsymbol{\xi})\rangle &= 0 \\
&= \langle\nabla_{\boldsymbol{\xi}}\psi(\boldsymbol{\xi})|\psi(\boldsymbol{\xi})\rangle + \langle\psi(\boldsymbol{\xi})|\nabla_{\boldsymbol{\xi}}\psi(\boldsymbol{\xi})\rangle \\
&= 2\,\mathrm{Re}\,\langle\psi(\boldsymbol{\xi})|\nabla_{\boldsymbol{\xi}}\psi(\boldsymbol{\xi})\rangle
\end{aligned}$$

$$\begin{array}{rll}
& \langle\psi(\boldsymbol{\xi})|\nabla_{\boldsymbol{\xi}}\psi(\boldsymbol{\xi})\rangle & \text{purely imaginary} \\
\boldsymbol{\mathcal{A}}(\boldsymbol{\xi}) = i & \langle\psi(\boldsymbol{\xi})|\nabla_{\boldsymbol{\xi}}\psi(\boldsymbol{\xi})\rangle & \text{real}
\end{array} \tag{1}$$

Last but not least:

What about time-reversal invariant systems?

Berry connection vs. perturbation theory

$$
\begin{aligned}
& |\psi_0(\boldsymbol{\xi}+\Delta\boldsymbol{\xi})\rangle - |\psi_0(\boldsymbol{\xi})\rangle \\
\simeq \quad & \sum_{n\neq 0}{}' |\psi_n(\boldsymbol{\xi})\rangle \frac{\langle\psi_n(\boldsymbol{\xi})|\,[\,H(\boldsymbol{\xi}+\Delta\boldsymbol{\xi}) - H(\boldsymbol{\xi})\,]\,|\psi_0(\boldsymbol{\xi})\rangle}{E_0(\boldsymbol{\xi}) - E_n(\boldsymbol{\xi})}
\end{aligned}
$$

$$
|\partial_\alpha \Psi_0(\boldsymbol{\xi})\rangle = \sum_{n\neq 0}{}' |\Psi_n(\boldsymbol{\xi})\rangle \frac{\langle\Psi_n(\boldsymbol{\xi})|\partial_\alpha H(\boldsymbol{\xi})|\Psi_0(\boldsymbol{\xi})\rangle}{E_0(\boldsymbol{\xi}) - E_n(\boldsymbol{\xi})}
$$

$$
\mathcal{A}_\alpha(\boldsymbol{\xi}) = i\langle\psi_0(\boldsymbol{\xi})|\partial_\alpha\psi_0(\boldsymbol{\xi})\rangle = 0
$$

"parallel transport" gauge

Berry connection vs. perturbation theory, better

$$
\begin{aligned}
|\Delta\psi_0(\xi)\rangle &= {\sum_{n\neq 0}}' |\psi_n(\xi)\rangle \frac{\langle\psi_n(\xi)|\,[\,H(\xi+\Delta\xi) - H(\xi)\,]\,|\psi_0(\xi)\rangle}{E_0(\xi) - E_n(\xi)} \\
|\psi_0(\xi+\Delta\xi)\rangle &\simeq |\psi_0(\xi)\rangle + |\Delta\psi_0(\xi)\rangle
\end{aligned}
$$

Better:

$$
\begin{aligned}
|\psi_0(\xi+\Delta\xi)\rangle &\to [\,|\psi_0(\xi)\rangle + |\Delta\psi_0(\xi)\rangle\,]\, \mathrm{e}^{-i\Delta\varphi(\xi)} \\
&\simeq [1 - i\,\Delta\varphi(\xi)\,]\,|\psi_0(\xi)\rangle + |\Delta\psi_0(\xi)\rangle
\end{aligned}
$$

$$
\begin{aligned}
\mathcal{A}(\xi)\cdot d\xi &= i\langle\psi_0(\xi)|\nabla_{\xi}\psi_0(\xi)\rangle \cdot d\xi \\
&= 0 \quad + \quad d\varphi
\end{aligned}
$$

Berry curvature: perturbation theory is OK

The Berry curvature is **gauge invariant**

$$\begin{aligned}\boldsymbol{\Omega}(\boldsymbol{\xi}) &= \nabla_{\boldsymbol{\xi}} \times \boldsymbol{\mathcal{A}}(\boldsymbol{\xi}) \qquad (\boldsymbol{\xi} \in \mathbb{R}^3) \\ &= i{\sum_{n\neq 0}}' \frac{\langle\psi_0(\boldsymbol{\xi})|\nabla H(\boldsymbol{\xi})|\psi_n(\boldsymbol{\xi})\rangle \times \langle\psi_n(\boldsymbol{\xi})|\nabla H(\boldsymbol{\xi})|\psi_0(\boldsymbol{\xi})\rangle}{[E_0(\boldsymbol{\xi}) - E_n(\boldsymbol{\xi})]^2}\end{aligned}$$

$\boldsymbol{\Omega}(\boldsymbol{\xi})$ **singular at degeneracy points**

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\end{aligned}
$$

$\boldsymbol{\Omega}(\boldsymbol{\xi})$ **singular at degeneracy points**

Stokes' theorem: $C = \partial\Sigma$

$$\gamma = \oint_{\partial\Sigma} \boldsymbol{\mathcal{A}}(\boldsymbol{\xi}) \cdot d\boldsymbol{\xi} = \int_{\Sigma} \boldsymbol{\Omega}(\boldsymbol{\xi}) \cdot \mathbf{n} \, d\sigma$$

.......only if Σ is **simply connected!**

Berry phase

- Loop integral of the Berry connection on a closed path:

$$\gamma = \oint_C \mathcal{A}(\xi) \cdot d\xi$$

- Berry phase, gauge invariant modulo 2π
- corresponds to **measurable** effects

Main message of Berry's 1984 paper:

- In quantum mechanics, **any** gauge-invariant quantity is potentially a physical observable

Coupling to "the rest of the Universe"

- γ cannot be cast as the expectation value of **any** Hermitian operator: instead, it is a gauge-invariant **phase** of the wavefunction

- The quantum system is **not** isolated:
  the parameter ξ summarizes the effect of "the rest of the Universe"
- **Slow variables:** ξ (e.g., a nuclear coordinate).
  Fast variables: here, the electronic coordinates
- For a genuinely isolated system, no Berry phase occurs and all observable effects **are** indeed expectation values of some operators
- What about classical mechanics?

Semantics: why "Geometric"?

So far, everything **time-independent**.
Suppose instead that:

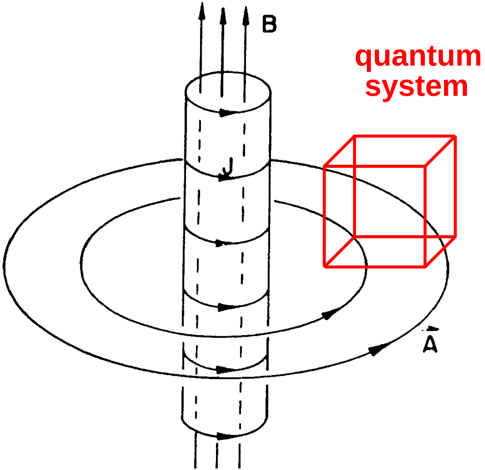
- The energy of $|\psi(\xi)\rangle$ is $E(\xi)$
- The parameter moves **adiabatically** on the closed path in time t: $\xi \rightarrow \xi(t)$, with $\xi(T) = \xi(0)$

Then the state acquires a total phase factor $\mathrm{e}^{i\gamma}\mathrm{e}^{i\alpha(T)}$

- The phase γ is independent of the details of motion: hence **"geometric"**
- The additional phase is the **"dynamical phase"**, and does depend on the motion: $\alpha(T) = -\frac{1}{\hbar}\int_0^T dt\, E(\xi(t))$

Outline

A quantum system in zero field



The parameter ξ

No magnetic field, box centered at the origin:

$$\left[\frac{1}{2}p^2 + V(\mathbf{r})\right]\chi(\mathbf{r}) = \varepsilon\chi(\mathbf{r}), \qquad \chi(\mathbf{r}) \quad \textbf{real} \text{ function}$$

Parameter $\xi \to$ the box position: $\qquad H(\mathbf{R}) = \frac{1}{2}p^2 + V(\mathbf{r} - \mathbf{R})$

$$\langle \mathbf{r}|\psi(\mathbf{R})\rangle = \chi(\mathbf{r} - \mathbf{R})$$

If there is a magnetic field (somewhere):

$$H(\mathbf{R}) = \frac{1}{2}[\,\mathbf{p} + \frac{e}{c}\mathbf{A}(\mathbf{r})\,]^2 + V(\mathbf{r} - \mathbf{R})$$

$$\langle \mathbf{r}|\psi(\mathbf{R})\rangle = \mathrm{e}^{-i\varphi(\mathbf{r})}\chi(\mathbf{r} - \mathbf{R})$$

$$\varphi(\mathbf{r}) = \frac{e}{\hbar c}\int_{\mathbf{R}}^{\mathbf{r}} \mathbf{A}(\mathbf{r}') \cdot d\mathbf{r}'$$

Berry connection & Berry phase

Formal solution!

However: In the region where $\mathbf{B}(\mathbf{r})$ vanishes, $\varphi(\mathbf{r})$ is a single valued function of $\mathbf{r}$, and $\langle\mathbf{r}|\psi(\mathbf{R})\rangle$ is an "honest" electronic wavefunction.

What about the dependence on the "slow" parameter $\mathbf{R}$?

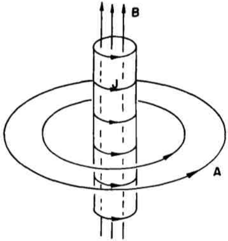
Berry connection:

$$i\langle\psi(\mathbf{R})|\nabla_{\mathbf{R}}\psi(\mathbf{R})\rangle = i\langle\chi(\mathbf{R})|\nabla_{\mathbf{R}}\chi(\mathbf{R})\rangle - \frac{e}{\hbar c}\mathbf{A}(\mathbf{R})$$

Berry phase:

$$\gamma = -\frac{e}{\hbar c}\oint_C \mathbf{A}(\mathbf{R})\cdot d\mathbf{R}$$

A closer look at the Berry phase γ



$$\gamma = -\frac{e}{\hbar c}\oint_C \mathbf{A}(\mathbf{R}) \cdot d\mathbf{R} = -\frac{e}{\hbar c}\Phi$$

- In this problem (and **only** in this problem):
  The “geometric vector potential” coincides with the magnetic vector potential (times a constant)

- $\frac{e}{hc}$ is the “flux quantum”: $\gamma = -2\pi\frac{\Phi}{\Phi_0}$
- Only the **fractional** part of Φ/Φ_0 is relevant
- The Berry phase γ is **observable** (mod 2π)

Bottom line (no paradox!)

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Reexamining the Born-Oppenheimer approximation

$$\mathcal{H}([\mathbf{R}],[\mathbf{x}]) = -\sum_j \frac{\hbar^2}{2M_j}\nabla^2_{\mathbf{R}_j} + H_{\mathrm{el}}([\mathbf{R}],[\mathbf{x}])$$

$[\mathbf{x}]$: electronic degrees of freedom (orbital & spin)
$[\mathbf{R}]$: nuclear coordinates $\mathbf{R}_j$
$-i\hbar\nabla_{\mathbf{R}_j}$: canonical nuclear momenta

$$\begin{aligned} H_{\mathrm{el}}([\mathbf{R}],[\mathbf{x}]) &= \text{electronic kinetic energy} \\ &+ \text{electron-electron interaction} \\ &+ \text{electron-nuclear interaction} \\ &+ \text{nuclear-nuclear interaction} \end{aligned}$$

Recipe

- Product ansatz: $\Psi([\mathbf{R}],[\mathbf{x}]) = \langle\, [\mathbf{x}]\,|\Psi_{\rm el}([\mathbf{R}])\rangle\, \Phi([\mathbf{R}])$
- Solve the electronic Schrödinger equation at **fixed** $\mathbf{R}_j$:

$$H_{\rm el}([\mathbf{R}],[\mathbf{x}])\,\langle\, [\mathbf{x}]\,|\Psi_{\rm el}([\mathbf{R}])\rangle = E_{\rm el}([\mathbf{R}])\,\langle\, [\mathbf{x}]\,|\Psi_{\rm el}([\mathbf{R}])\rangle$$

- Use $E_{\rm el}([\mathbf{R}])$ as the potential energy for nuclear motion:

$$\left(-\sum_j \frac{\hbar^2}{2M_j}\nabla^2_{\mathbf{R}_j} + E_{\rm el}([\mathbf{R}])\right)\Phi([\mathbf{R}]) = E\,\Phi([\mathbf{R}])$$

- **Textbook example:** Vibrational levels of a biatomic molecule.
- On many occasions, the nuclear motion can be considered as **purely classical** (Schrödinger $\longrightarrow$ Newton).

A closer look at the Born-Oppenheimer recipe

- Product ansatz: $\Psi([\mathbf{R}],[\mathbf{x}]) = \langle\, [\mathbf{x}] \,|\Psi_{\rm el}([\mathbf{R}])\rangle\, \Phi([\mathbf{R}])$
- The operator $\nabla_{\mathbf{R}_j}$ acting on $\Psi([\mathbf{R}],[\mathbf{x}])$:

$$\begin{aligned}\nabla_{\mathbf{R}_j}\Psi([\mathbf{R}],[\mathbf{x}]) \quad &= \quad \langle\, [\mathbf{x}] \,|\Psi_{\rm el}([\mathbf{R}])\rangle \nabla_{\mathbf{R}_j}\Phi([\mathbf{R}]) \\ &+ \quad \langle\, [\mathbf{x}] \,|\nabla_{\mathbf{R}_j}\Psi_{\rm el}([\mathbf{R}])\rangle \Phi([\mathbf{R}])\end{aligned}$$

- Multiplying by $\langle\Psi_{\rm el}([\mathbf{R}])\,|\,[\mathbf{x}]\,\rangle$ and integrating in $d[\mathbf{x}]$:

$$\begin{aligned}&\int d[\mathbf{x}] \quad \langle\Psi_{\rm el}([\mathbf{R}])\,|\,[\mathbf{x}]\,\rangle \nabla_{\mathbf{R}_j}\Psi([\mathbf{R}],[\mathbf{x}]) \\ &= \quad \left(\nabla_{\mathbf{R}_j} + \langle\, \Psi_{\rm el}([\mathbf{R}])\,|\nabla_{\mathbf{R}_j}\Psi_{\rm el}([\mathbf{R}])\rangle\right)\Phi([\mathbf{R}])\end{aligned}$$

- **Nuclear kinetic energy**, after $[\mathbf{x}]$ is "integrated out":

$$\mathcal{T}_{\rm N} = \sum_j \frac{\hbar^2}{2M_j}\left(-i\hbar\nabla_{\mathbf{R}_j} - i\hbar\langle\, \Psi_{\rm el}([\mathbf{R}])\,|\nabla_{\mathbf{R}_j}\Psi_{\rm el}([\mathbf{R}])\rangle\right)^2$$

A term was missing!

- Naive Born-Oppenheimer approximation:

$$\Big(\mathcal{T}_\mathrm{N} + E_\mathrm{el}([\mathbf{R}])\Big)\,\Phi([\mathbf{R}]) = E\,\Phi([\mathbf{R}]), \qquad \mathcal{T}_\mathrm{N} = -\sum_j \frac{\hbar^2}{2M_j}\nabla^2_{\mathbf{R}_j}$$

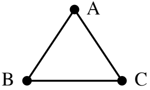
- More accurate Born-Oppenheimer approximation:

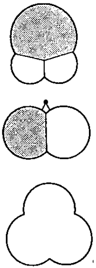
$$\mathcal{T}_\mathrm{N} = \sum_j \frac{1}{2M_j}\Big(-i\hbar\nabla_{\mathbf{R}_j} - i\hbar\langle\, \Psi_\mathrm{el}([\mathbf{R}])\,|\nabla_{\mathbf{R}_j}\Psi_\mathrm{el}([\mathbf{R}])\rangle\Big)^2$$

- The electronic **Berry connection** acts as a “geometric vector potential” in the nuclear Hamiltonian

- In most cases the correction is neglected: **Why?**

The hydrogen (or sodium) trimer, LCAO





$$|2\rangle = \frac{1}{\sqrt{6}}\left(|B\rangle + |C\rangle - 2\,|A\rangle \right)$$

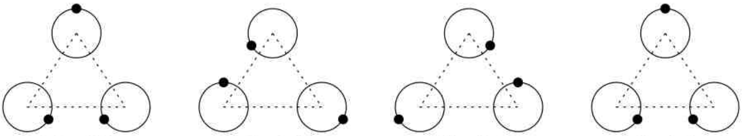
$$|1\rangle = \frac{1}{\sqrt{2}}\left(|C\rangle - |B\rangle \right)$$

$$|0\rangle = \frac{1}{\sqrt{3}}\left(|A\rangle + |B\rangle + |C\rangle \right)$$

- Equilateral geometry, 3 valence electrons: degenerate HOMO ($\varepsilon_1 = \varepsilon_2$)
- Broken-symmetry equilibrium geometry: **isosceles** Jahn-Teller splitting ($\varepsilon_1 \neq \varepsilon_2$)

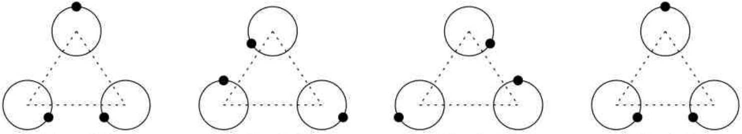
$|1\rangle$ is the HOMO, $|2\rangle$ is the LUMO

Born-Oppenheimer surfaces

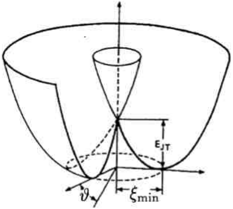


pseudorotation

Born-Oppenheimer surfaces



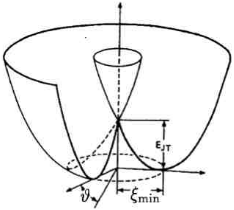
pseudorotation



“conical intersection”

a.k.a. “diabolical point”

Nuclear dynamics



$$E_{\rm el}(\boldsymbol{\xi}) = E_{\rm el}(\xi) \qquad \vartheta\text{-independent}$$
$$E_{\rm el}(\xi) = \frac{1}{2}k(\xi^2 \pm 2\,\xi_{\min}\,\xi)$$

Lowest BO surface:

minimum in $\xi_{\min}$

$$E_{\rm el}(\xi_{\min}) = -\frac{1}{2}k\,\xi_{\min}^2 = -E_{\rm JT}$$

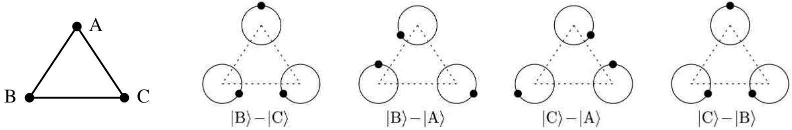
- **Classical:** Free motion at valley's bottom, $M = 3m$ & transverse oscillations
- **Quantized pseudorotations:**

$$\Phi_{mn}(\xi,\vartheta) \propto H_n(\alpha\xi)\,\mathrm{e}^{-\frac{\omega}{2}(\xi-\xi_{\min})^2}\,\mathrm{e}^{im\vartheta}$$

$m \in \mathbb{Z}, \qquad n = 0, 1, 2, \ldots$

Ground state: m=0, n=0

H. C. Longuet-Higgins et al. (1958)

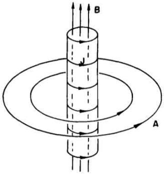


The **electronic** wfn $\langle \mathbf{r} | \psi_{\rm el}(\xi) \rangle$ **changes sign** (a π phase)
The **total** wfn $\Psi(\xi, \mathbf{r}) = \langle \mathbf{r} | \psi_{\rm el}(\xi) \rangle \, \Phi(\xi)$ must be **single-valued**
Even the **nuclear** wfn must change sign

$\Rightarrow$ **Different quantization rules!**

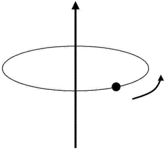
$\Phi_{mn}(\xi, \vartheta) \propto H_n(\alpha \xi) \, \mathrm{e}^{-\frac{\omega}{2}(\xi - \xi_{\rm min})^2} \, \mathrm{e}^{im\vartheta}$
m **half-integer**, $n = 0, 1, 2, \ldots$
Ground state: $m = \frac{1}{2}, n = 0$
Observable effect in **QM**, no effect in **CM**
(the system **does not visit** the conical intersection)

Molecular Aharonov-Bohm effect



Aharonov-Bohm effect (**real B field**):

$$\gamma = \oint_C \mathcal{A}(\xi) \cdot d\xi = -2\pi \frac{\Phi}{\Phi_0} \mod 2\pi$$



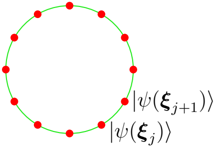
Molecular Aharonov-Bohm effect ($\mathbf{B} = 0$):

$$\gamma = \oint_C \mathcal{A}(\xi) \cdot d\xi = \pi \mod 2\pi$$

Same as having a δ-like flux tube at the conical intersection

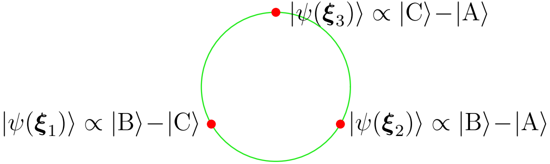
$$\Phi = \frac{\Phi_0}{2}$$ (**half-quantum**, a.k.a. "π flux")

Berry phase: discrete algorithm



$$\begin{aligned} \gamma &= \sum_{j=1}^{N} \Delta\varphi_{j,j+1} \\ &= - \operatorname{Im} \log \langle\psi(\boldsymbol{\xi}_1)|\psi(\boldsymbol{\xi}_2)\rangle\langle\psi(\boldsymbol{\xi}_2)|\psi(\boldsymbol{\xi}_3)\rangle \dots \langle\psi(\boldsymbol{\xi}_N)|\psi(\boldsymbol{\xi}_1)\rangle \end{aligned}$$

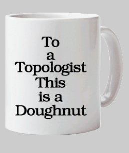
$N = 3$

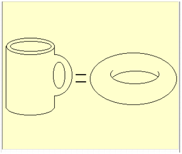


$$\langle\psi(\boldsymbol{\xi}_1)|\psi(\boldsymbol{\xi}_2)\rangle\langle\psi(\boldsymbol{\xi}_2)|\psi(\boldsymbol{\xi}_3)\rangle\langle\psi(\boldsymbol{\xi}_3)|\psi(\boldsymbol{\xi}_1)\rangle = -\frac{1}{8}$$

Outline

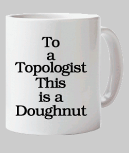
What topology is about

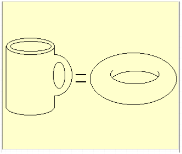




Topological invariant: **genus** (=1 here)

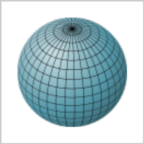
What topology is about





Topological invariant: **genus** (=1 here)

From Wikipedia:



genus 0

genus 1

genus 2

genus 3

Topology & conical intersections

Herzberg & Longuet-Higgins, 1963:

It shows that a conically self-intersecting potential surface has a different topological character from a pair of distinct surfaces which happen to meet at a point. Indeed, if an electronic wave function changes sign when we move round a closed loop in configuration space, we can conclude that somewhere inside the loop there must be a singular point at which the wave function is degenerate; in other words, there must be a genuine conical intersection, leading to an upper or lower sheet of the surface, as the case may be.

Berry phase γ

- Topologically trivial: $\gamma = 0 \text{ mod } 2\pi = \pi \times (0 \text{ mod } 2)$
- Topologically nontrivial: $\gamma = \pi \text{ mod } 2\pi = \pi \times (1 \text{ mod } 2)$
- Topological **invariant** $\in \mathbb{Z}_2$
  ($\mathbb{Z}_2$ = additive group of the integers mod 2)

Robustness of the topological invariant

Two-valued topological invariant:
The $\mathbb{Z}_2$ index is either 0 or 1 (mod 2)

- The index is robust against deformations of the path C, provided it does not cross the "obstruction"
- The index is very robust against **continuous** deformations of Hamiltonian & wave function, provided the HOMO-LUMO gap does not close
- We can even "continuously deformate" the wfn into the exact correlated one (if ground state non degenerate)
- Key role of **time-reversal invariance**
- In modern jargon:
  $\mathbb{Z}_2$ invariant is **"protected"** by time-reversal symmetry

Outline

BO approx. for the H atom, $\mathbf{B} = 0$

$$
\begin{aligned}
\mathcal{H}(\mathbf{R},\mathbf{r}) &= -\frac{\hbar^2}{2M}\nabla^2_{\mathbf{R}} + H_{\rm el}(\mathbf{R},\mathbf{r}) \\
H_{\rm el}(\mathbf{R},\mathbf{r}) &= -\frac{\hbar^2}{2m}\nabla^2_{\mathbf{r}} - \frac{e^2}{|\mathbf{r}-\mathbf{R}|}
\end{aligned}
$$

Lowest BO surface:

$$
E_{\rm el}(\mathbf{R}) = \text{const} \;= -\frac{e^2}{2a_0}, \qquad \langle \mathbf{r}|\psi_{\rm el}(\mathbf{R})\rangle \propto \mathrm{e}^{-|\mathbf{r}-\mathbf{R}|/a_0}
$$

BO Recipe: $$-\frac{\hbar^2}{2M}\nabla^2_{\mathbf{R}}\Phi(\mathbf{R}) - \frac{e^2}{2a_0}\Phi(\mathbf{R}) = E\Phi(\mathbf{R})$$

$$
E_{\rm BO}(\mathbf{k}) = \frac{\hbar^2 k^2}{2M} - \frac{e^2}{2a_0}, \qquad \Psi_{\rm BO}(\mathbf{R},\mathbf{r}) \propto \mathrm{e}^{-|\mathbf{r}-\mathbf{R}|/a_0}\ \mathrm{e}^{i\mathbf{k}\cdot\mathbf{R}}
$$

Compare exact with Born-Oppenheimer approx.

$$\mathcal{H}(\mathbf{R},\mathbf{r}) = -\frac{\hbar^2}{2M}\nabla^2_{\mathbf{R}} - \frac{\hbar^2}{2m}\nabla^2_{\mathbf{r}} - \frac{e^2}{|\mathbf{r}-\mathbf{R}|}$$

Separable using: $\tilde{\mathbf{R}} = \dfrac{M\,\mathbf{R} + m\,\mathbf{r}}{M+m}, \quad \tilde{\mathbf{r}} = \mathbf{r} - \mathbf{R}$

$$\begin{aligned}
E(\mathbf{k}) &= \frac{\hbar^2 k^2}{2(M+m)} - \frac{\mu e^2}{2a_0}, \qquad \mu = \frac{m\,M}{m+M} \\
E_{\mathrm{BO}}(\mathbf{k}) &= \frac{\hbar^2 k^2}{2M} - \frac{e^2}{2a_0} \\
\lim_{m/M\to 0} E(\mathbf{k}) &= E_{\mathrm{BO}}(\mathbf{k})
\end{aligned}$$

Compare exact with Born-Oppenheimer approx.

$$\mathcal{H}(\mathbf{R},\mathbf{r}) = -\frac{\hbar^2}{2M}\nabla^2_{\mathbf{R}} - \frac{\hbar^2}{2m}\nabla^2_{\mathbf{r}} - \frac{e^2}{|\mathbf{r}-\mathbf{R}|}$$

Separable using: $\tilde{\mathbf{R}} = \dfrac{M\,\mathbf{R} + m\,\mathbf{r}}{M+m}, \quad \tilde{\mathbf{r}} = \mathbf{r} - \mathbf{R}$

$$\begin{aligned}
E(\mathbf{k}) &= \frac{\hbar^2 k^2}{2(M+m)} - \frac{\mu e^2}{2a_0}, \qquad \mu = \frac{m\,M}{m+M} \\
E_{\mathrm{BO}}(\mathbf{k}) &= \frac{\hbar^2 k^2}{2M} - \frac{e^2}{2a_0}, \qquad k \ll \frac{1}{a_0} \\
\lim_{m/M\to 0} E(\mathbf{k}) &= E_{\mathrm{BO}}(\mathbf{k})
\end{aligned}$$

BO approx. for the H atom, $\mathbf{B} \neq 0$

(Neglecting irrelevant spin-dependent terms)

$$\begin{aligned}
\mathcal{H}(\mathbf{R},\mathbf{r}) &= \frac{1}{2M}\left[-i\hbar\nabla_{\mathbf{R}} - \frac{e}{c}\mathbf{A}(\mathbf{R})\right]^2 + H_{\rm el}(\mathbf{R},\mathbf{r}) \\
H_{\rm el}(\mathbf{R},\mathbf{r}) &= \frac{1}{2m}\left[-i\hbar\nabla_{\mathbf{r}} + \frac{e}{c}\mathbf{A}(\mathbf{r})\right]^2 - \frac{e^2}{|\mathbf{r}-\mathbf{R}|}
\end{aligned}$$

In a **constant** **B** field $\quad E_{\rm el}(\mathbf{R}) = E_{\rm el} = \text{const}$

Naive recipe: $$\frac{1}{2M}\left[-i\hbar\nabla_{\mathbf{R}} - \frac{e}{c}\mathbf{A}(\mathbf{R})\right]^2\Phi(\mathbf{r}) - E_{\rm el}\,\Phi(\mathbf{r}) = E\Phi(\mathbf{r})$$

- Same kinetic energy **as if** the proton were "naked"
- Classical limit: the H atom is deflected by a Lorentz force
- A neutral system is **not** deflected by a Lorentz force

Solution of the paradox

"Screened" Born-Oppenheimer approximation:
Schmelcher, Cederbaum, & Meyer, 1988

Better:
Berry Connection & Berry curvature (same as for $\mathbf{B} = 0$)

$$\frac{1}{2M}\left[-i\hbar\nabla_{\mathbf{R}} - \frac{e}{c}\mathbf{A}(\mathbf{R})\right]^2 \to \frac{1}{2M}\left[-i\hbar\nabla_{\mathbf{R}} - \frac{e}{c}\mathbf{A}(\mathbf{R}) - \hbar\boldsymbol{\mathcal{A}}(\mathbf{R})\right]^2$$

- $\mathbf{A}(\mathbf{R})$ genuine vector potential of magnetic origin
- $\boldsymbol{\mathcal{A}}(\mathbf{R}) = i\langle\psi_{\mathrm{el}}(\mathbf{R})|\nabla_{\mathbf{R}}\psi_{\mathrm{el}}(\mathbf{R})\rangle$ Berry connection

Detailed reckoning in the central gauge

$$
\begin{aligned}
H_{\rm el}(\mathbf{R},\mathbf{r}) &= \frac{1}{2m}\left[-i\hbar\nabla_{\mathbf{r}} - \frac{e}{2c}\mathbf{B}\times\mathbf{r}\right]^2 - \frac{e^2}{|\mathbf{r}-\mathbf{R}|} \\
H_{\rm el}(0,\mathbf{r}) &= \frac{1}{2m}\left[-i\hbar\nabla_{\mathbf{r}} + \frac{e}{2c}\mathbf{B}\times\mathbf{r}\right]^2 - \frac{e^2}{r} \\
\langle\mathbf{r}|\psi_{\rm el}(0)\rangle &= \tilde{\psi}_0(\mathbf{r}) \qquad \text{complex wfn, cylindrical symmetry}
\end{aligned}
$$

$$
\langle\mathbf{r}|\psi_{\rm el}(\mathbf{R})\rangle = \mathrm{e}^{-\frac{ie}{2\hbar c}\mathbf{r}\cdot\mathbf{B}\times\mathbf{R}}\;\tilde{\psi}_0(|\mathbf{r}-\mathbf{R}|)
$$

$$
\mathcal{A}(\mathbf{R}) = i\langle\psi_{\rm el}(\mathbf{R})|\nabla_{\mathbf{R}}\psi_{\rm el}(\mathbf{R})\rangle = -\frac{e}{2\hbar c}\mathbf{B}\times\mathbf{R} = -\frac{e}{\hbar c}\mathbf{A}(\mathbf{R})
$$

$$
\mathcal{T}_{\rm N} = \frac{1}{2M}\left[-i\hbar\nabla_{\mathbf{R}} - \frac{e}{c}\mathbf{A}(\mathbf{R}) - \hbar\mathcal{A}(\mathbf{R})\right]^2 = \frac{\hbar^2}{2M}\nabla^2_{\mathbf{R}}
$$

Magnetic & geometric together

- **H atom**
  - Paradox solved (both quantum nucleus & classical nucleus)
  - In the classical limit **no Lorentz force**
  - **Hamiltonian** (quantum & classical)
    The Berry **connection** cancels the **vector potential**
  - **Newton Eq.** (gauge invariant):
    The Berry **curvature** cancels the **magnetic field**

- **Molecule** (rotations & vibrations in a **B** field)
  - The two terms **do not cancel**
  - They are of the same order of magnitude
  - The geometric term is important even for classical nuclei:
    "geometric Lorentz force" in Newton Eq.

$\mathbf{B} = 0$ vs. $\mathbf{B} \neq 0$ in Born-Oppenheimer

- $\mathbf{B} = 0$ (time-reversal symmetric)
  - Conical intersections $\Rightarrow$ nontrivial geometric effects
  - The electronic wfn **can** be chosen as **real**
  - The Berry **curvature** vanishes (or is singular)
  - Classical nuclei **not affected** by geometric effects
  - The Berry phase only shows up when quantising the nuclei
- $\mathbf{B} \neq 0$ (time-reversal symmetry absent)
  - No singularity needed in the Born-Oppenheimer surface
  - The electronic wfn must be **complex**
  - The Berry **curvature** is generally **nonzero**
  - Classical nuclei **are affected** by geometric effects
  - The Berry curvature enters the Newton Eq. for the nuclei